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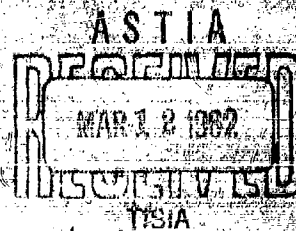
ARF Project D217

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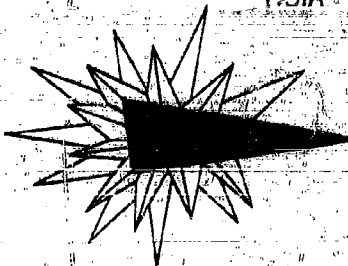
INHIBITION OF FLASHING OF AEROSOLS

Quarterly Progress Report VII

R. Kamo



25 years of research



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DA-18-108-405-CML-777

Quarterly Progress Report No. VII

October 15, 1961 to January 14, 1962

INHIBITION OF FLASHING OF AEROSOLS

R. Kamo

February 21, 1962

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This seventh Quarterly Progress Report summarizes the work performed during the past quarter, from October 15, 1961 to January 14, 1962, under Contract No. DA-18-108-405-CML-777, on the study of "Inhibition of Flashing of Aerosols", for the Physical Chemistry Division of the Army Chemical Center, Edgewood, Maryland.

The following personnel have contributed to this project during the seventh quarter: C. C. Miesse, D. K. Werle, and R. Kamo.

Data and all pertinent information are recorded in Armour Research Foundation Logbooks C-10313 and C-11642.

Respectfully submitted,

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R. Kamo, Principal Investigator

APPROVED:



T. H. Schiffman, Assistant Director of
Fluid Dynamics and Propulsion Research

RK/aa

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INHIBITION OF FLASHING OF AEROSOLS

I. ABSTRACT

This seventh quarterly progress report covers the period from October 15, 1961 to January 14, 1962, during which time the lean flammability limits and the upward flame propagation velocities of dibutyl and dimethyl phthalates were determined. The effect of nucleation with sodium chloride was also investigated. Spontaneous ignition temperatures were determined for dimethyl phthalate and dibutyl phthalate and several additives.

The lean flammability limits of dibutyl and dimethyl phthalates were found to be approximately the same for various droplet size. However, the flame propagation velocities of dimethyl phthalate were found to be lower than that for dibutyl phthalate. The spontaneous ignition temperature of dimethyl phthalate (601°C) was also found to be considerably higher than that of dibutyl phthalate (247°C).

Sodium chloride nucleated dibutyl phthalate apparently shows some tendency towards increasing the lean flammability limits. As for the effect of additive, some of the pyrophoric compounds such as iron pentacarbonyl, and triethyl aluminum exhibits excellent inhibiting qualities.

II. INTRODUCTION

This project under Contract DA-18-108-405-CML-777 was initiated on April 15, 1960, by the Army Chemical Center to investigate fundamental behavior in the flashing of flammable liquid aerosols so that means of prevention or inhibition of the flashing may be revealed.

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The variables to be investigated include mass concentration, drop size, liquid volatility, ignition source, and, if possible, pressure and temperature. In the second phase of this study, flame inhibiting additives will be investigated.

During the seventh quarter, the lean flammability limits and the upward flame propagation velocities were determined for dimethyl and dibutyl phthalate. The effect of nucleation of dibutyl phthalate with sodium chloride was also studied. Spontaneous ignition temperatures of dimethyl phthalate and dibutyl phthalate with several additives were determined in the newly constructed spontaneous ignition apparatus. The experimental techniques, laboratory data, discussion of results and plans for future work are presented herein.

III. EXPERIMENTAL TECHNIQUES

The laboratory combustion apparatus was adequately illustrated and its operations described in our earlier report. During the seventh quarter, two additional pieces of laboratory equipment were constructed and utilized during the course of our investigation; namely, the flame propagation velocity detector, and a closed cup spontaneous ignition temperature apparatus.

A. Flame Propagation Velocity Detector

Flame propagation velocities were also measured by an electric timer which was actuated by two photocell relays in series, such that the flame, in passing the first photocell, closed the timer circuit, and subsequently opened the timer circuit in passing the second photocell. The photoelectronic relays were modified to operate on filtered DC

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voltage rather than 60 cycle AC voltage such that the response time was reduced to less than 5 milliseconds.

B. Spontaneous Ignition Temperature Apparatus

These ignition temperatures were determined in an electrically heated five-inch diameter by five-inch high brass block, containing a two-inch diameter by two and one-half inch deep recess. Except for the slightly larger cup used here, the metal block is similar to that described in NACA Technical Note 2547⁽²⁾. Block temperatures were measured with a chromel-alumel thermocouple at the base of the ignition cup. The test procedure followed was identical to that described in the above report except that all ignitions were conducted at an air flow rate of 25 cc/min. Dropwise and spray injection procedures described in NACA Technical Note 2848⁽³⁾ were also used here except that a simplified spray injector was used in preference to the cumbersome device described in the latter report. The spray injector used here consisted of a type P-20 fog nozzle (Bete Fog Nozzle, Inc., Greenfield, Massachusetts) machined down to a 0.4-inch diameter by 0.4-inch high cylinder soldered to an adapter mounted on a 1 cc hypodermic syringe.

IV. TEST DATA

During the seventh quarter period considerable amount of experimental data on lean flammability limits, flame propagation velocities and spontaneous ignition temperatures were obtained for the phthalate compound. The effect of additives with these compounds was also investigated. The phthalate group was selected after studying the physical and chemical properties of the phosphate and phthalate compounds. The results of our investigation are presented in the

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following paragraphs.

A. Properties of Phthalates and Phosphate Compounds

In order to study the effects of volatility with a chemically similar series of compounds, the phthalates and the phosphates were examined for vapor pressure variation with temperature and for flash point, as well as density and viscosity, as shown in Figs. 1 and 2, and Table I. The source of information is also indicated in Table I.

B. Lean Flammability Limits and Flame Propagation Velocity

The first eighteen (18) test runs on the lean flammability limits of dibutyl phthalate DBP were reported in Table II of our sixth quarterly progress report. Subsequently, the flame propagation velocities were also determined for the first eighteen runs. The results of the flame propagation velocities for these earlier tests are shown in Table II. Test Runs No. 19 to 29 indicated in Table II show additional lean flammability limits and flame propagation velocities for DBP. The data represents results for DBP droplets ranging from 8 to 280 microns arithmetic mean diameter.

Table III of this report shows the lean flammability limits and the flame propagation velocities for dimethyl phthalate. The arithmetic mean diameter of the DMP aerosols covered in this series of tests ranged from 41 to 150 microns.

Table IV shows the eleven (11) test runs obtained for dibutyl and dimethyl phthalate covering the size range of 8 to 300 microns. Aerosols in Test Runs No. 40 to 47 inclusive were nucleated with sodium chloride. The data indicated again the lean limits of flammability as well as the upward flame propagation velocities.

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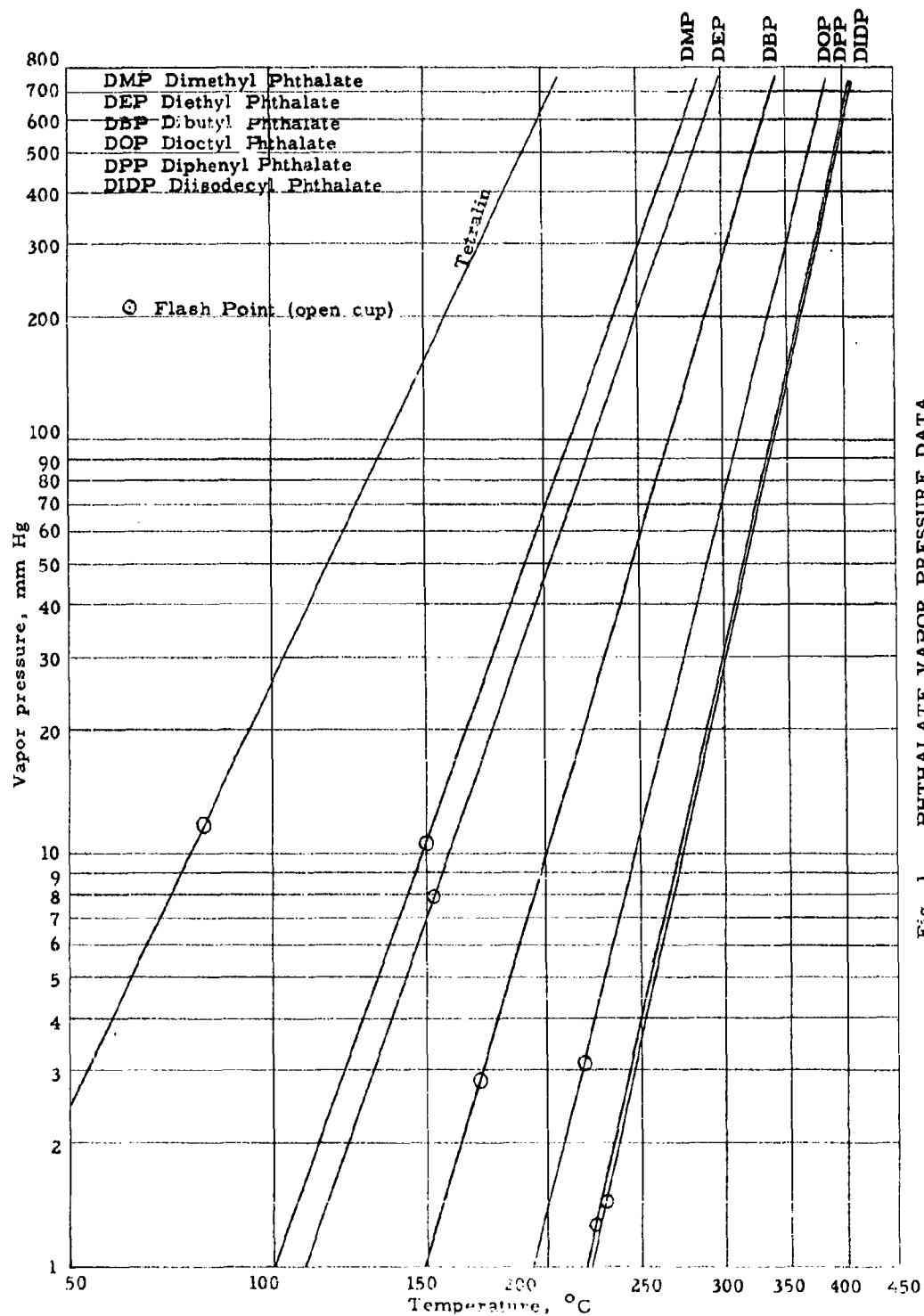


Fig. 1 PHTHALATE VAPOR PRESSURE DATA

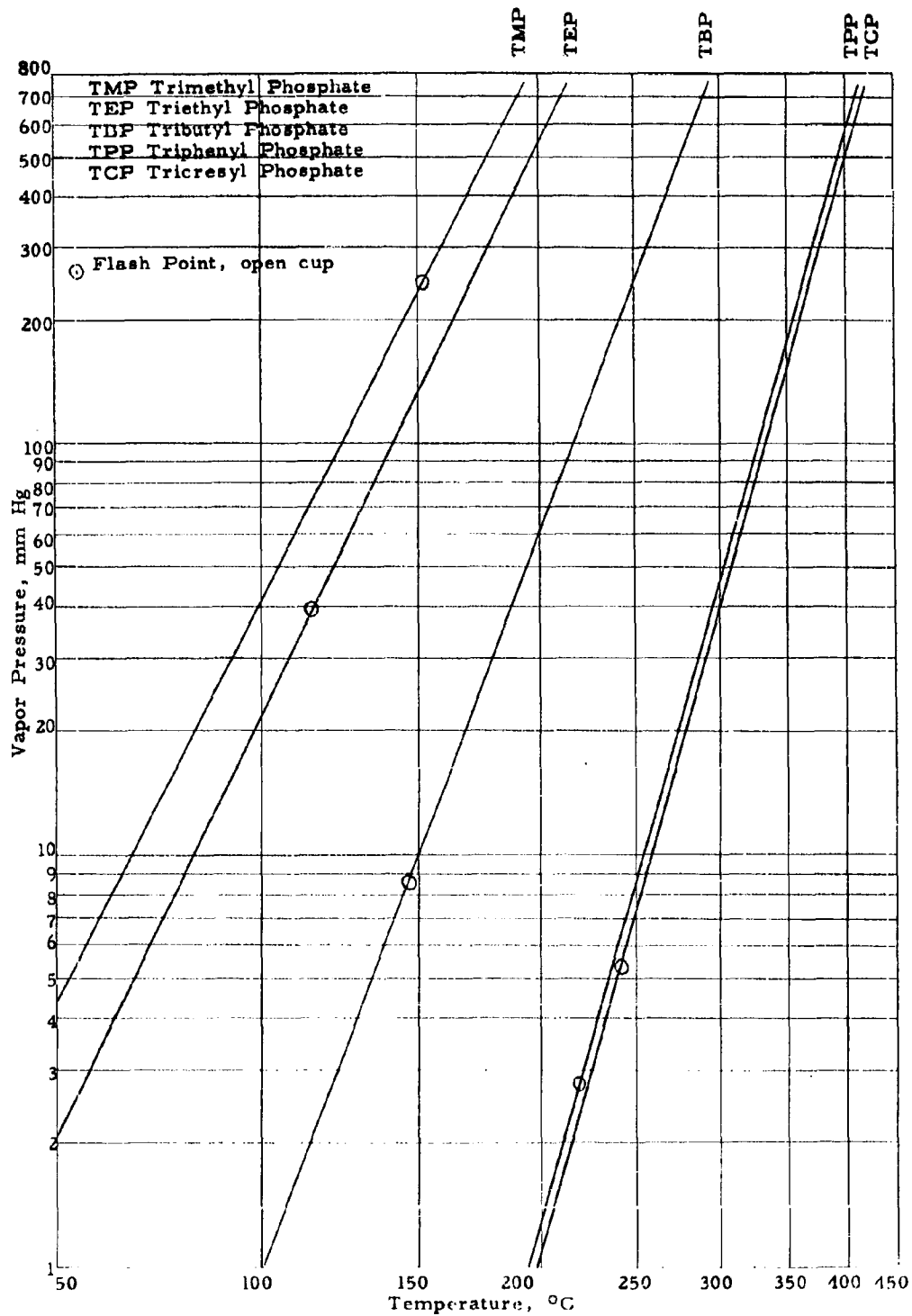


Fig. 2 PHOSPHATE VAPOR PRESSURE DATA

Table I
PHYSICAL PROPERTIES OF PHOSPHATE AND PHTHALATE COMPOUNDS

	Density, gm/ml	Viscosity, cs at 70°F	Boiling Point, °C	Flash Point, Open Cup °C	Source
Dimethyl phthalate	1.189	13.6	282	149	Monsanto
Diethyl phthalate	1.121	12.0	298	152	Monsanto
Dibutyl phthalate	1.048	18	340	171	Monsanto
Dioctyl phthalate	0.982	107	386	218	Monsanto
Diphenyl phthalate	1.28	Solid (to 69°C)	405	224	Monsanto
Diisodecyl phthalate	0.965	145	415	232	Monsanto
Tetralin	0.973	--	207	82	Fisher Scientific
Trimethyl phosphate	1.197	2.5	197	152	Ethyl Corp.
Triethyl phosphate	1.068	1.7	215	115	Eastman Chemi- cal Company
Tributyl phosphate	0.976	3.4	289	146	Commercial Solvents
Triphenyl phosphate	1.268	60/20 Solid (to 49°C)	370	225	Monsanto
Tricresyl phosphate	1.162	130	420	243	Monsanto

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Table II

LEAN FLAMMABILITY LIMITS AND FLAME PROPAGATION VELOCITY
DATA FOR DIBUTYL PHTHALATE DROPLETS RANGING FROM
8 TO 280 MICRONS ARITHMETIC MEAN DIAMETER

Test No.	Diameter, microns			Lean Limit, mg/l	Upward Propagation, cm/sec
	Arith. Mean	Mass	Median		
19	190		226	17.0	---
20	211		236	33.2	---
21	155		199	22.2	---
22	256		306	40.0	---
23	261		322	39.3	---
24	172		207	24.1	47.0
25	166		205	25.7	45.9
26	222		299	28.9	41.3
27	224		312	30.0	40.3
28	255		407	31.7	35.7
29	242		384	29.3	32.8
1, 2, 3	81*		117*	---	44.2
4, 5, 6	76*		104*	---	45.0
7, 8, 9	118*		132*	---	46.5
10, 11, 12	37*		77*	---	38.4
13, 14, 15	7.8*		8.6*	---	34.1
17, 18	280*		356*	---	36.6

* Average of tests previously reported

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Table III

LEAN FLAMMABILITY LIMITS AND FLAME PROPAGATION VELOCITY
DATA FOR DIMETHYL PHTHALATE DROPLETS RANGING FROM
41 TO 150 MICRONS ARITHMETIC MEAN DIAMETER

Test No.	Diameter, microns			Lean Limit mg/l	Upward Propagation cm/sec
	Arith. Mean	Mass	Median		
30	68		88	22.9	38.9
31	64		81	25.3	40.7
32	64		79	26.8	41.3
33	67		80	21.3	42.1
34	131		153	20.9	39.8
35	125		137	23.8	38.3
36	150		182	22.7	37.3
37	42		168	37.1	35.6
38	43		119	34.8	36.8
39	41		126	34.1	35.7

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Table IV

LEAN FLAMMABILITY LIMITS AND FLAME PROPAGATION VELOCITIES
FOR DIBUTYL AND DIMETHYL PHTHALATES SHOWING THE EFFECT
OF NUCLEATION WITH SODIUM CHLORIDE

Test No.	Aerosol	Diameter, microns			Lean limit, mg/l	Upward Propagation ^{***} , cm/sec
		Arith. Mean	Mass	Median		
40	DMP	11.2		14.2	92.0	80.1
41	DMP	10.6		13.3	94.3	76.1
42	DMP	6.2		7.9	104	93.6
43	DMP	6.3		8.0	105	97.5
44	DMP	6.1		7.9	106	104.7
45	DBP [*]	8.4		10.4	88.9	109.5
46	DBP [*]	8.9		11.1	93.7	114.9
47	DBP [*]	9.0		11.2	84.1	124.4
48	DMP	228		313	28.6	34.7
49	DMP	217		292	32.2	36.7
50	DMP	220		292	32.0	38.5

*Strong sodium line color observed on ignition in these tests - aerosols in tests 40-47 were nucleated with sodium chloride.

**In tests 40-47 the propagation velocities are for the portion of propagation which presented a continuous flame front, hence the large values.

C. Spontaneous Ignition Data

Table V shows the spontaneous ignition temperature data obtained for the dibutyl and dimethyl phthalates. Whether data is based on dropwise or spray addition to the apparatus, is noted on the table. The effect of various additives and their concentration with dibutyl phthalate are shown also in Table V. It is seen that the spontaneous ignition temperature of dimethyl phthalate is considerably higher than that of dibutyl phthalate. The addition of additives noted in Table V to dibutyl phthalate never exceeded the spontaneous ignition temperature of pure dimethyl phthalate.

V. DISCUSSION OF RESULTS

Based on the results of the physical and chemical properties of the phosphate and phthalate compounds shown in Figs. 1 and 2 and Table I, the phthalate group was selected for investigation.

The phosphate compounds have the disadvantages of high flash points and widely varying vapor pressure at the flash points. Also, the pronounced self-nucleating effect previously observed for bis (2-ethylhexyl) hydrogen phosphite may also be characteristic of the phosphates in which case it would not be possible to use the thermal generator to produce drops larger than about 20 microns. The vapor pressure values at the flash points for dimethyl - through dioctyl phthalate are all low and reasonably close together whereas the flash point temperatures range from 149°C to 218°C and the boiling points range from 282°C to 386°C. The above considerations led to the tentative selection of dimethyl-, dibutyl-, and dioctyl phthalates for investigating the effect of volatility of high boiling liquids on combustion properties.

Table V
MEASURED SPONTANEOUS IGNITION TEMPERATURES

Simulant	Additive, mol. per cent	Spontaneous ignition temp., closed cup, 25 cc air/min., °C	Remarks
DBP	None	247	Spray addition
DBP	Bromine, 5%	254	Spray addition
DBP	1, 2, 3 tribromopropane, 5%	253	Spray addition
DBP	dicyclohexylamine, 5%	264	Spray addition
DBP	triethanolamine titanate, 5%	257	Spray addition
DBP	carbon disulfide	255	Spray addition
DBP	triethyl aluminum, 5%	270	Spray addition
DBP	triethyl aluminum, 11.8%	541	Dropwise addition, spray did not ignite
DBP	trimethyl phosphate, 5%	255	Spray addition
DBP	trimethyl phosphate, 10%	256	Spray addition
DBP	---	438	Dropwise addition
DBP	CB _r ₄ , 5%	249	Spray addition, flame observed to ignition tem- perature
DBP	CB _r ₄ , 50%	254	Spray addition, flame observed to ignition tem- perature
DBP	F E(Co) ₅ , 5%	526	Dropwise addition, spray did not ignite
DBP	---	601	Dropwise addition, spray did not ignite

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The combustion data for dibutyl and dimethyl phthalates and additives were presented in Section IV of this report. The lean flammability limits and flame propagation velocities for these phthalate compounds and additives are shown graphically in Figs. 3,4,5,6,7, and 8 of this report.

A. Flammability Limits

The results of the current series of lean limit tests, using the large drop generator (Nos. 19-29), are given in Table II. Ignition of these aerosols at the lean limit was difficult, and, as a result, the lean limit data are somewhat scattered when plotted against the mass median diameter (MMD) as seen in Fig. 3. It is noted that the U-shaped curve previously reported is unaltered by the additional data. The plot of the lean limit versus arithmetic mean diameter (AMD) in Fig. 4 shows less scatter, particularly in the larger drop size range. This deviation was especially noticeable in Tests 28 and 29 in which there was an exceptionally wide spread of drop sizes as indicated by the large difference between the AMD and the MMD. Thus, the lean limit appears to correlate better with the AMD than with the MMD as the aerosol becomes more heterogeneous.

The lean limit and propagation velocity data for DMP are presented in Table II and Fig. 5. As with dibutyl phthalate (DBP) data, the lean limit data are less scattered when plotted against the AMD (arithmetic mean diameter) than when plotted against the MMD (mass median diameter). This was especially true in tests 37, 38, and 39 for which a wide range of drop sizes was present as indicated by the large difference between the AMD and the MMD. The heterogeneous character of the aerosols in the latter three tests was due to inadequate

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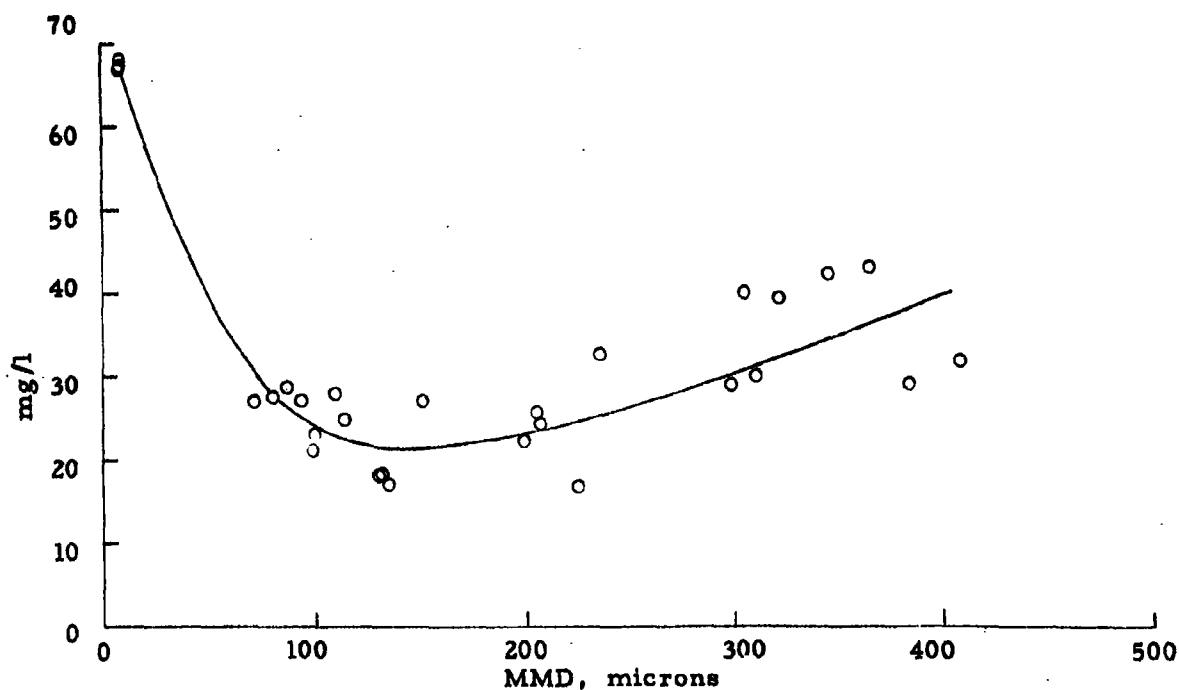


Fig. 3 DBP LEAN LIMIT VS MASS MEDIAN DIAMETER, MMD

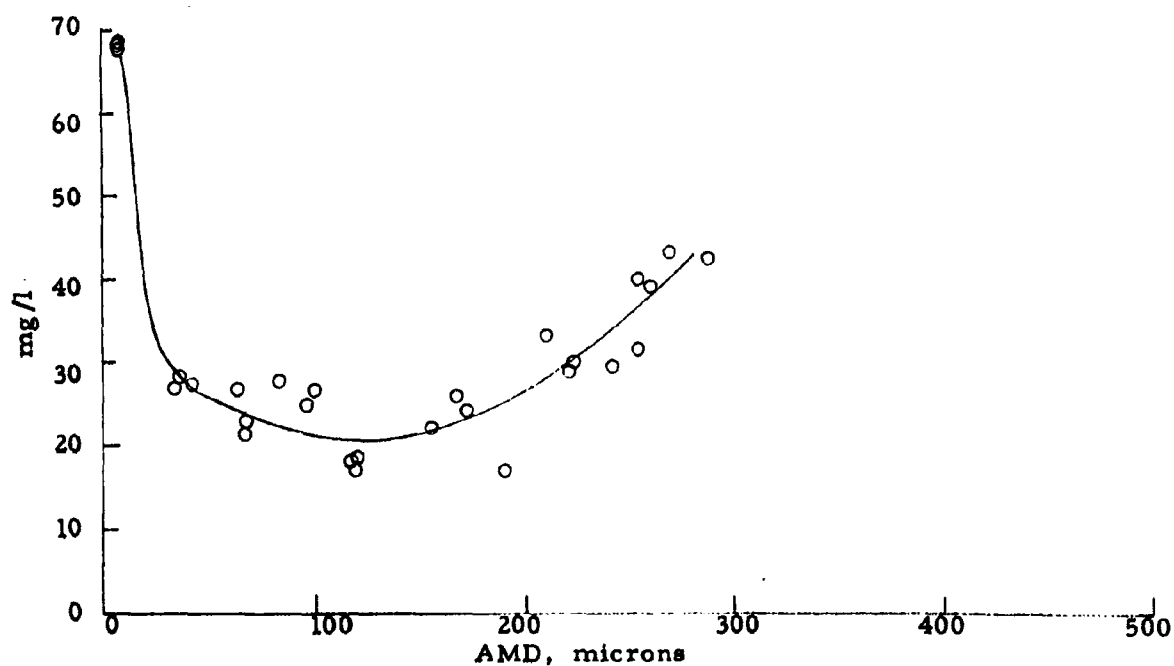


Fig. 4 DBP LEAN LIMIT VS ARITHMETIC MEAN DIAMETER, AMD

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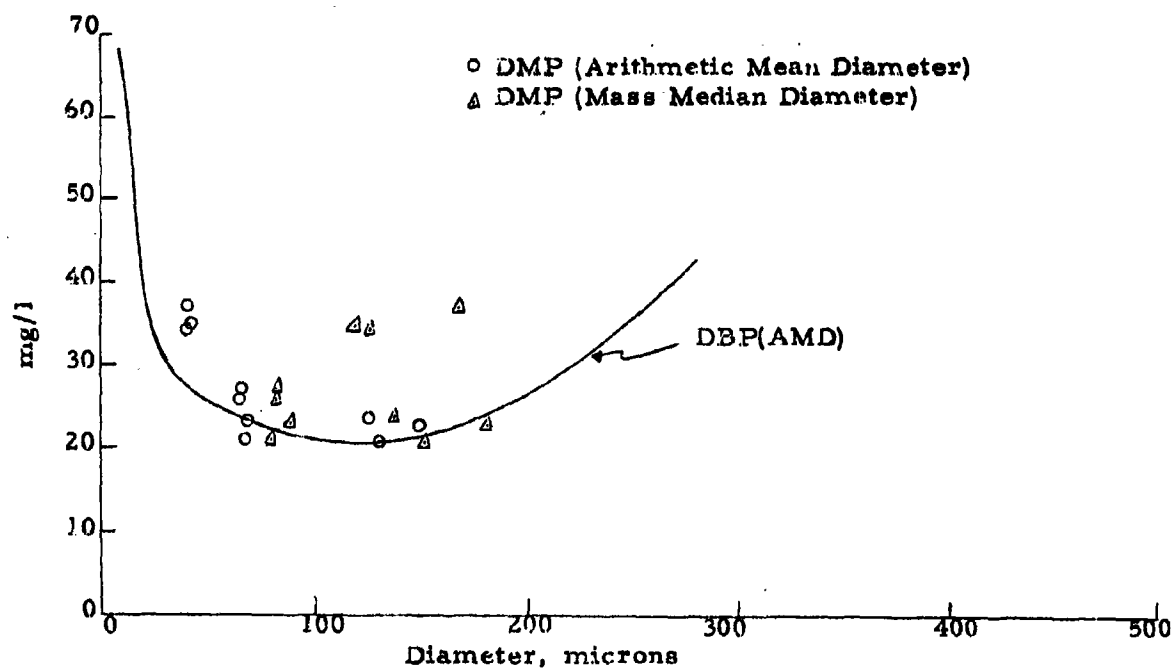


Fig. 5 LEAN LIMIT VS DROP DIAMETER

nucleation. Apparently the gold nuclei are not as effective for DMP condensation as for DBP condensation. Subsequently, additional tests were performed with more effective nuclei, such as sodium chloride. While volatile metal salts have been shown to have an inhibiting effect on flames, the mass concentration of the nuclei will be exceedingly small and should not produce a measurable effect on the lean limit determination.

The lean limit and propagation velocity data are presented in Table IV and Fig. 6. It is now apparent that the lean limit curves for DBP and DMP are very nearly the same except that DMP tends toward a slightly higher lean limit in the 6 to 50 micron range. This is in line with the fact that the small drop aerosols approach continuous flame front burning as the drop size diminishes, and DMP, being more volatile than DBP, as well as having a higher spontaneous ignition temperature, vaporizes more completely before ignition can occur. Thus the percentage of relatively vapor-free voids in the aerosol flame front should diminish with increasing volatility, and the effect should be more pronounced as the distance between drops decreases and more area is available for evaporation, i.e., as the aerosol drop size is reduced.

It follows then, that a less volatile aerosol (such as DOP) should tend toward a lower lean limit in the 6 to 50 micron size range. This effect may be cancelled out, however, by other variables, such as the spontaneous ignition temperature. Subsequent tests with DOP during the last quarter may clear up this point.

In tests 40-47, nucleation was effected with sodium chloride due to the relative ineffectiveness of the gold nuclei for DMP condensation.

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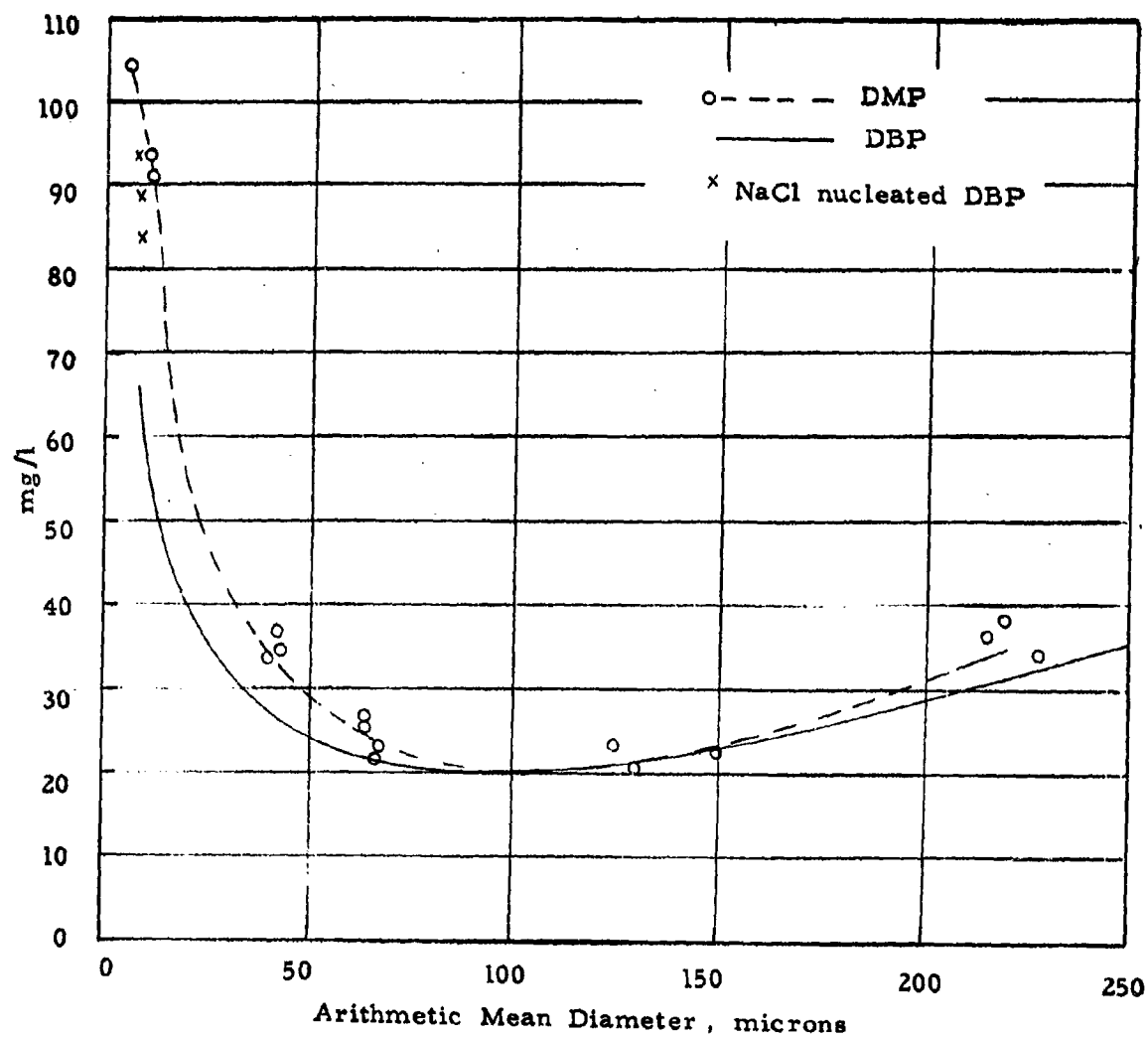


Fig:6 LEAN LIMIT OF FLAMMABILITY VERSUS DROP DIAMETER
OF DMP, DBP, AND NaCl NUCLEATED DBP

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In order to determine the effect, if any, of sodium chloride on the lean limit, tests 45-47 were conducted with sodium chloride nucleated DBP to compare the lean limit determined in tests 13-15 with the gold nucleated DBP. Apparently the sodium chloride does increase the lean limit, but it should be noted that the lean limit curve rises steeply (almost asymptotically), in this region, such that a small change in drop size results in a large change in the lean limit. Hence, any errors in drop size measurement are magnified. In all of the tests conducted with sodium chloride nucleated aerosols, the Armour Research Foundation particle counter was used to determine size distributions, since the coated slide technique is unsatisfactory for nucleated aerosols below about ten microns in size. The particle counter was calibrated with a monodisperse DOP aerosol before use in these tests.

B. Flame Propagation Velocities

The variation of the upward flame propagation velocity with DBP drop diameter is shown in Fig. 7. A maximum flame propagation velocity of 47 cm/sec occurred at an AMD of 140 microns or an MMD of 180 microns. It is interesting to note that the maximum upward flame propagation velocity occurs in the same size range as the minimum lean limit. The decrease in the upward propagation velocity for the drops above 150 microns is due, in part, to their high terminal settling velocity. The upward propagation velocity should approach zero as the drop terminal settling velocity approaches the drop to drop flame propagation rate. Thus, Burgoyne ⁽¹⁾ concluded that the critical size for upward propagation in a tube is of the order of 300 microns for tetralin. This also appears to be essentially true for DBP, although thermal convection effects were

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often noted in the burning of the larger drop aerosols such that the flame at times lunged upward on one side of the tube and at other times was virtually stationary. The measured upward propagation velocities, shown in Fig. 7, varied considerably for the largest drop aerosols, and each of the points shown is the average value of six or more measurements. As a result of the existence of gross convective currents and turbulence, it appears probable that upward propagation in an unconfined aerosol would extend to drops appreciably larger than 300 microns.

As noted in Fig. 8 the upward flame propagation velocities for DMP are somewhat lower than for DBP, apparently due to the much higher spontaneous ignition temperature of the former (see Table V for DMP data). Thus, the time interval for bringing DMP vapor surrounding a drop to the ignition temperature is lengthened by the requirement that the DMP vapor must be heated to 601°C for spontaneous ignition whereas DBP vapor will ignite spontaneously at 247°C .

Flame propagation velocities in tests 40-47 were higher than any previously reported measurements and indicate a complete transition from drop to drop propagation to a continuous flame front. Dropwise, propagation proceeds at a much lower rate due to the slow accumulation of heat associated with the low lean limit of the large drop aerosols. Ignition of the large drop aerosols invariably resulted in dropwise propagation up most of the five-foot combustion tubes. Ordinarily, however, the flame accelerated rapidly near the top of the tube apparently due to a gradual increase in temperature in the aerosol above the flame front. As the drop size decreased, the transition from the slow dropwise propagation to rapid continuous propagation took place nearer to the point of ignition at

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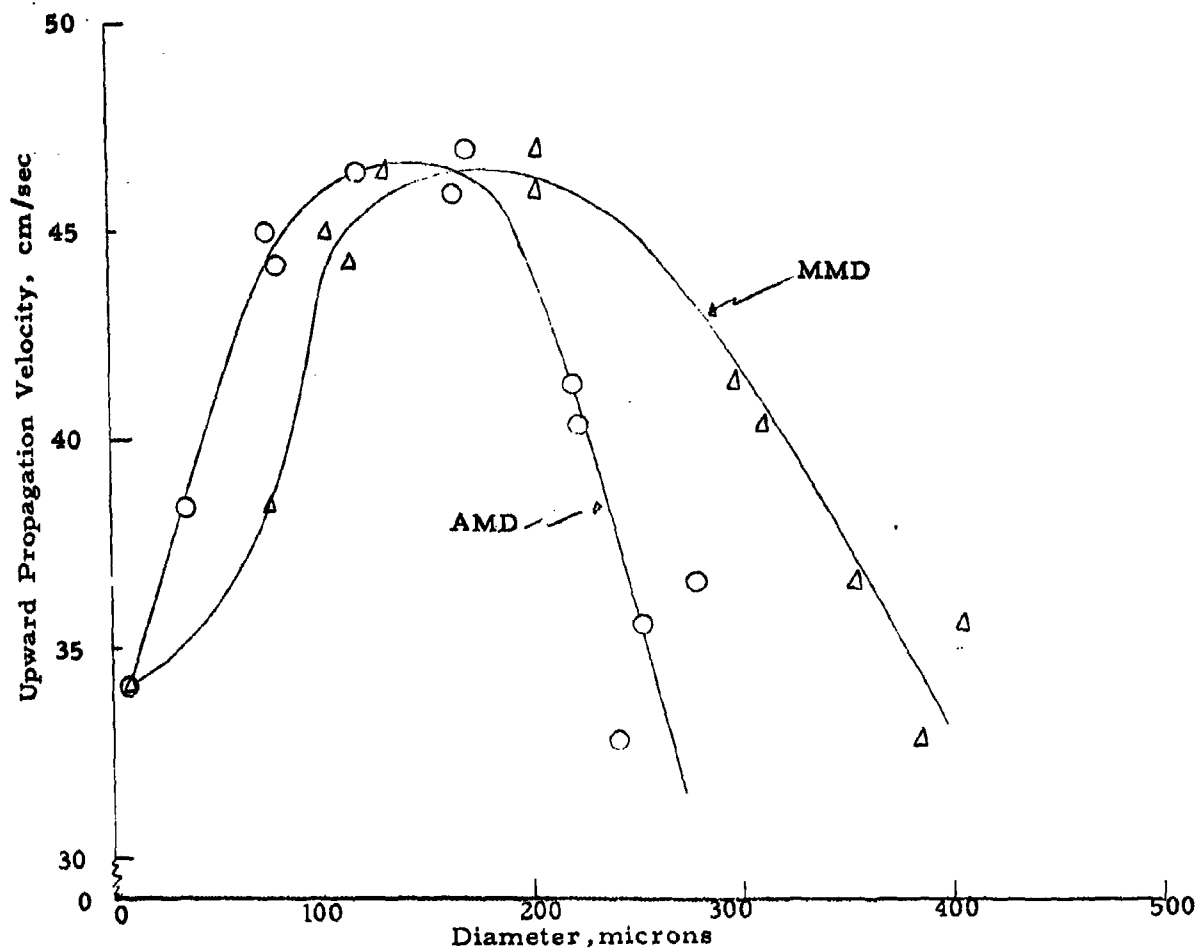


Fig. 7 UPWARD FLAME PROPAGATION VELOCITY
OF DBP

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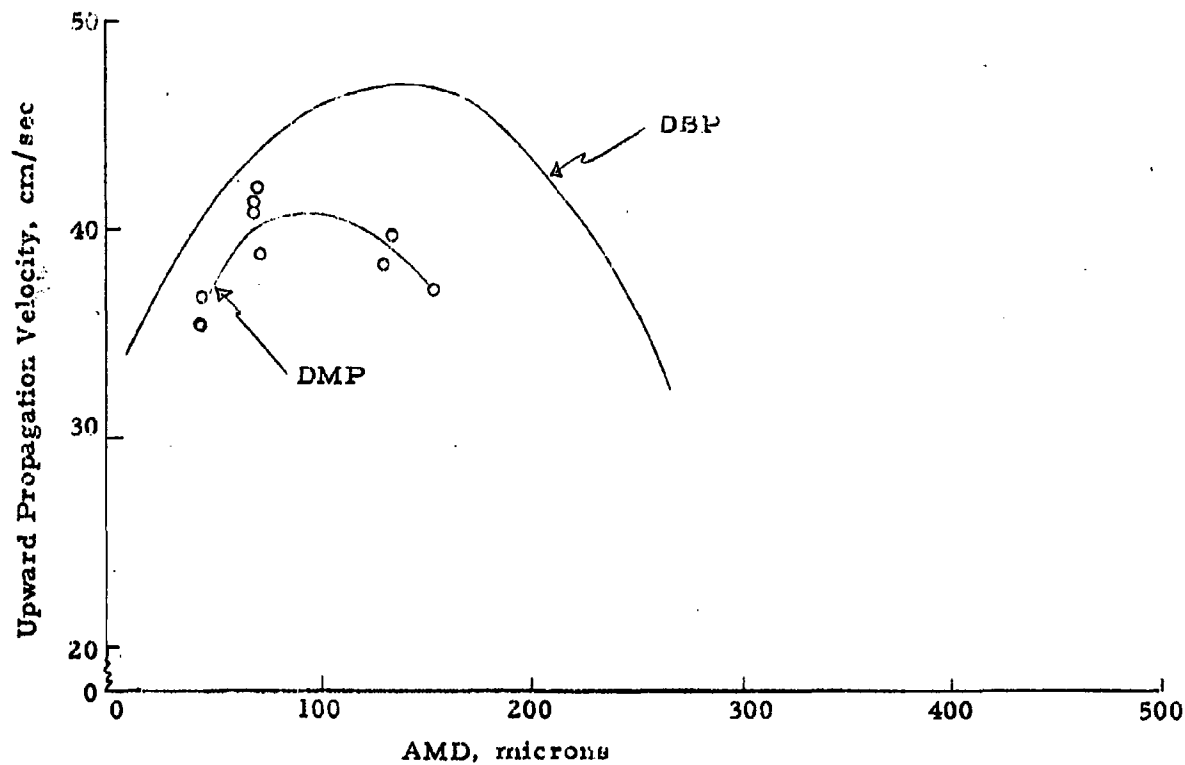


Fig. 8 UPWARD PROPAGATION VELOCITY FOR DMP AND DBP AEROSOLS

the bottom of the combustion tube. For a below 10 micron DBP or DMP aerosol, the flame propagated in a slow dropwise fashion for about the first foot of travel, after which a fast-travelling homogeneous flame front appeared which was accompanied by a roaring sound. Dropwise flame propagation was invariably quiet.

C. Spontaneous Ignition Temperatures

Spontaneous ignition temperature measurements have been made with the newly constructed furnace utilizing a hypodermic syringe-actuated spray for introduction of the liquid under test. Although the flammability limit and propagation velocity curves for DMP lie close to the corresponding DBP curves, it is noted that the spontaneous ignition temperature for the former is much higher. The results of the spontaneous ignition tests are shown in Table V.

The relative ineffectiveness of CBr_4 in raising the spontaneous ignition temperature of DBP confirms the observation of Frank, Blackham, and Swarts⁽³⁾ that the halogen-containing compounds are surprisingly ineffective as additives to the liquid as opposed to conventional fire extinguishing uses in which the halogen-containing compound is mixed with the air.

It is interesting to note that despite the fact that DMP has a spontaneous ignition temperature 354 degrees higher than that of DBP; the DMP lean limit curve is essentially the same as that for DBP. Differences may become apparent when data are obtained for aerosol sizes outside the 40 to 150 micron size range covered to date for DMP.

Some additional spontaneous ignition temperature tests have also been made on DBP containing various additives as shown in Table V. Of

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the additives tested, the most interesting is triethyl aluminum, a highly reactive pyrophoric liquid which, in the pure state, ignites on exposure to air, even at room temperature. However, when dissolved in DBP to the extent of 11.8 mol per cent, the spontaneous ignition temperature of DBP was elevated by nearly 300°C. Iron pentacarbonyl, also an effective inhibitor (Monthly Letter Report No. 15), is very nearly pyrophoric, and when undiluted can ignite spontaneously in air at temperatures as low as 44°C. While triethyl aluminum would probably not be a practical inhibitor because of its highly reactive nature, it does point to the use of an inhibitor which can and does react at relatively low temperatures. The spontaneous ignition temperature tests with halogenated hydrocarbon inhibitors indicate that they do not meet this requirement. Rosser, Wise and Miller⁽⁵⁾ pointed out that the relative thermal stability of alkyl bromides may be a factor in the reduced effectiveness of cool nitrogen oxide supported flames as compared to air supported flames. This may also be a factor in the present case where the inhibitor is incorporated with the simulant under test.

VI. CONCLUSIONS

As a result of the research investigation carried out during the seventh quarter, the following important conclusions can be drawn from the experimental data on the phthalate group and additives thereof:

1. Lean flammability limits correlate better with arithmetic mean diameter than with mass mean diameter, especially pronounced in the larger droplet aerosols.
2. The lean flammability limits of dibutyl and dimethyl phthalate are very nearly the same except that dimethyl

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tends toward a slightly high lean limit in the 6 to 50 micron size range.

3. The flame propagation velocity for DBP reaches a maximum of 47 cm/sec at an AMD of 140 microns and occurs in the same size range as the minimum lean flammability limit.
4. The upward flame propagation velocities for DMP are lower than that for DBP, supposedly due to the higher spontaneous ignition temperature.
5. The halogen-containing compounds are ineffective as additives to liquids in raising spontaneous ignition temperatures of DBP. (Some of the additives which raise the spontaneous ignition temperatures of DBP are pyrophoric in themselves.)

VII. SPONSOR VISIT

On 9 February 1962, Mr. J. V. Pistritto, Project Engineer from the Colloidal Branch visited the Armour Research Foundation to discuss the project on the "Inhibition of Flashing of Aerosols". Project progress as well as plans for the remaining period of the project were discussed with Messrs R. Kamo and D. Werle of Armour.

The work of Linuma, Penner, and Aerojet General was highly recommended to be considered in our analysis of the current program.

Other instructions from Mr. Pistritto included the following:

1. Submit any possible patentable ideas or equipment (patent disclosure forms left with Armour)
2. Submit draft of final report for approval before publication
3. Subjects to be covered in the final report
4. Send one additional copy of the final report.

VIII. PERSONNEL CHANGE

As of the end of the third quarter, January 31, 1962, Mr. C. C. Miesse terminated his employment at Armour Research Foundation. Thus, he is no longer available as principal investigator on ARF Project D217, "Inhibition of Flashing of Aerosols". Mr. R. Kamo who has had considerable experience in the droplet combustion field has been appointed temporarily to continue the role of principal investigator. It is hoped that the change is satisfactory and meets with the approval of the Sponsor. Notice to the above effect has been forwarded to the contracting officer in accordance with Contract DA-18-108-405-CML-777.

IX. PLANS FOR FUTURE WORK

The research program for the final period from 15 January 1962 to 14 April 1962 will be concluded with the investigation of dioctyl phthalate, which is less volatile than dibutyl phthalate. The lean flammability limit as well as the flame propagation velocities will be determined. This will complete the current study of the effect of volatility on the combustion properties of high boiling point simulants. Spontaneous ignition temperature measurements on inhibited system will continue as time and funds permit.

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